

CHEMISTRY

A **European** Journal

Supporting Information

Silicon(IV) Corroles

Giuseppe Pomarico,^[a] Donato Monti,^[a] Martina Bischetti,^[a] Andrea Savoldelli,^[a]
Frank R. Fronczek,^[b] Kevin M. Smith,^[b] Damiano Genovese,^[c] Luca Prodi,^[c] and
Roberto Paolesse^{*[a]}

chem_201801246_sm_miscellaneous_information.pdf

Author Contributions

M.B. NMR Studies: Lead.

Table of Contents

Synthetic protocols of PluS NPs with non covalently embedded 1 , 3 and 5	Table S1
UV-vis spectra of 4 and 5	Figure S1
¹ H NMR spectrum of 1 in CDCl ₃	Figure S2
¹ H NMR spectrum of 1 in DMSO	Figure S3
¹ H NMR spectrum of 1 in DMSO + Fluoride ions	Figure S4
¹ H NMR Titration of 1 in DMSO with Fluoride ions: β-pyrrolic region	Figure S5
¹ H NMR Titration of 1 in DMSO with Fluoride ions: axial –OH region	Figure S6
FAB mass spectrum of 1	Figure S7
¹ H NMR spectrum of 2 in CDCl ₃	Figure S8
FAB mass spectrum of 2	Figure S9
FAB mass spectrum of the products mixture after reaction of 2 with HCl.	Figure S10
¹ H NMR spectrum of 3 in CDCl ₃	Figure S11
¹⁹ F NMR spectrum of 3 in DMSO	Figure S12
FAB mass spectrum of 3	Figure S13
¹ H NMR spectrum of 4 in CDCl ₃	Figure S14
FAB mass spectrum of 4	Figure S15
¹ H NMR spectrum of 5 in DMSO	Figure S16
FAB mass spectrum of 5	Figure S17
UV-vis spectral variation of 1 upon F ⁻ titration	Figure S18
UV-vis spectral variation of 1 in the Q region upon F ⁻ titration	Figure S19
Comparison of the UV-vis spectral variations of 1 upon addition of F ⁻ (black line) and OH ⁻ (red dotted line)	Figure S20
Absorption spectra of PluS NPs doped with corroles 1 and 2 in water	Figure S21
Excitation spectra of PluS NPs doped with corroles 1 and 2 in water	Figure S22
Time Resolved Emission Spectroscopy (TRES) of NP3L in bidimensional map	Figure S23
Plot of decays of TRES	Figure S24
Emission anisotropy of samples NP1L , NP1H , NP3L and NP3H	Figure S25
Absorbance spectra before and 2 days after addition of NaF 50 mM to NP1L and NP2L	Figure S26
Emission spectra before and 2 days after addition of NaF 50 mM to NP1L and NP2L	Figure S27

Table S1. Synthetic protocols of PluS NPs with non covalently embedded 1, 3 and 5

Sample	Pluronic F127 (mg)	TEOS (μmol)	Si-corrole	Nominal doping (vs. TEOS) ratio mol	Si-corrole (μmol)	Si-corrole (mg)
NP1L	100	800	1-Low%	0.1%	0.73	0.45
NP1H	100	800	1-High%	0.25%	2.00	1.25
NP3L	100	800	3-Low%	0.1%	0.48	0.4
NP3H	100	800	3-High%	0.25%	2.98	2.5
NP5L	100	800	5-Low%	0.1%	0.39	0.5
NP5H	100	800	5-High%	0.25%	1.8	2.3

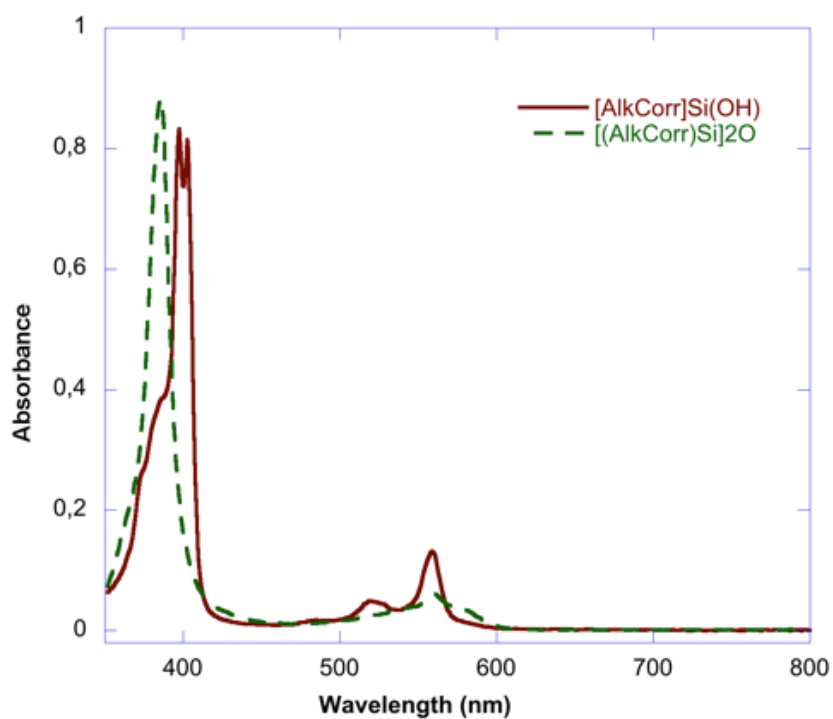


Figure S1. UV-vis spectra of monomer **4** (red full line) and dimer **5** (green dashed line).

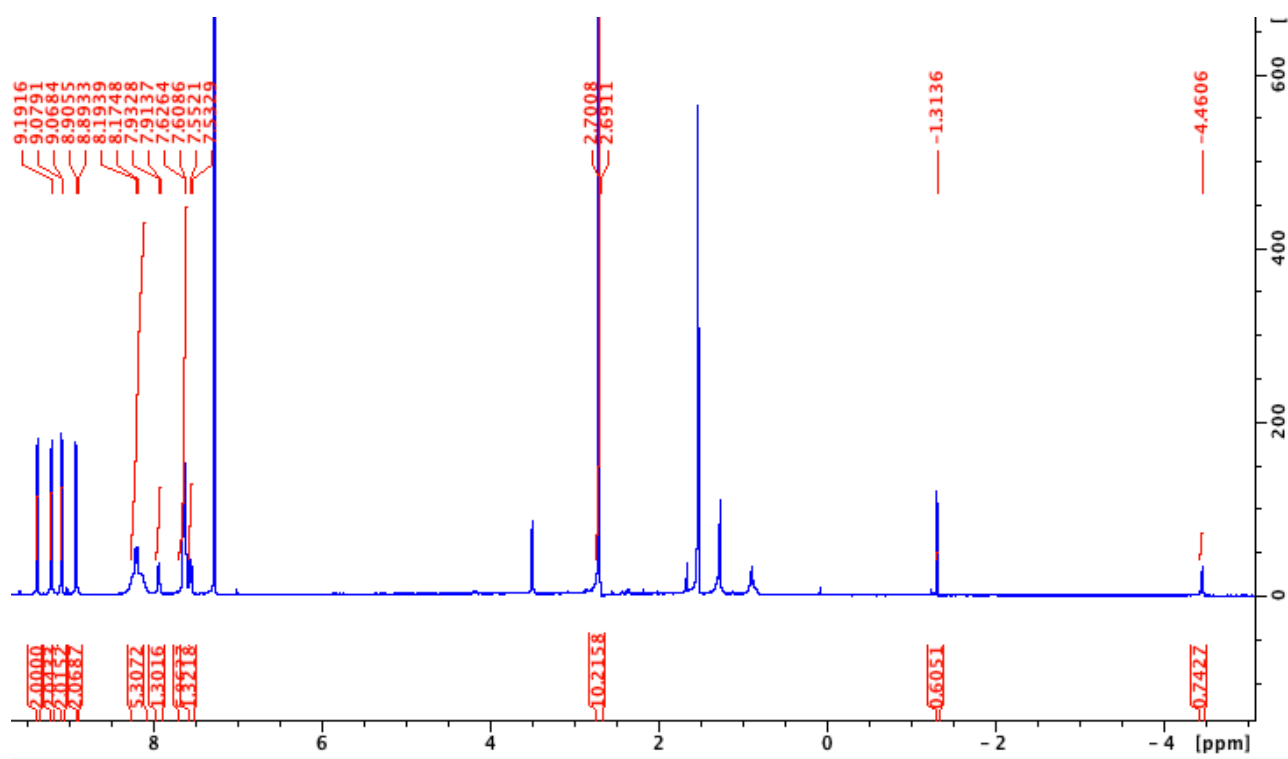


Figure S2. ^1H NMR spectrum of **1** in CDCl_3 .

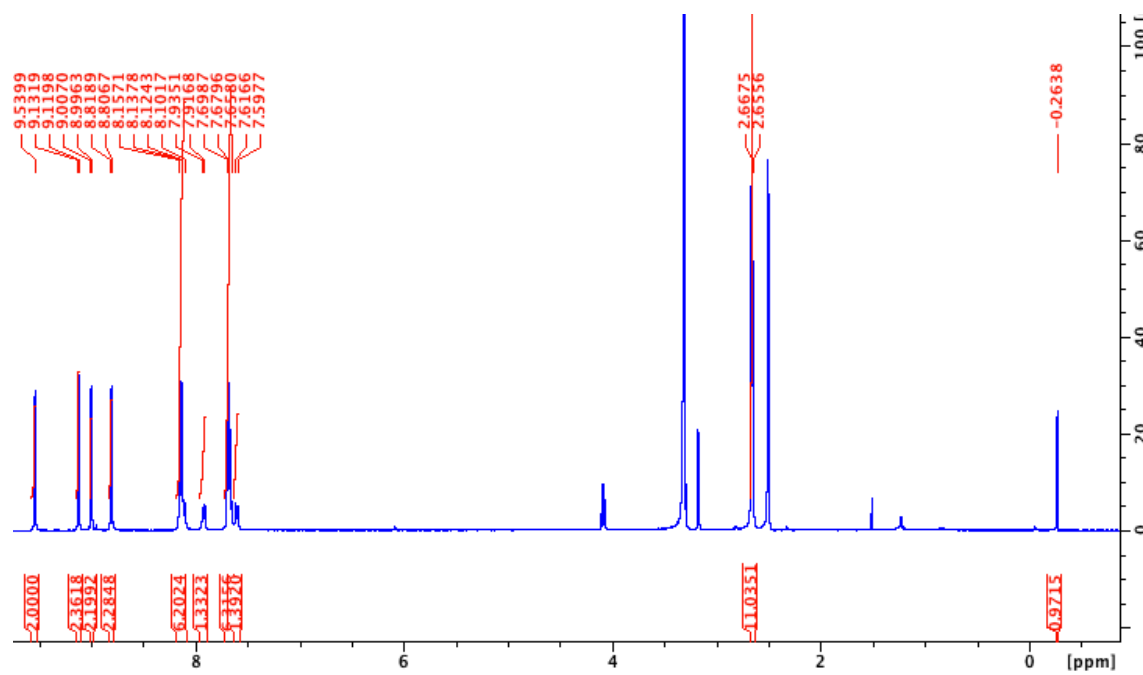


Figure S3. ^1H NMR spectrum of **1** in DMSO.

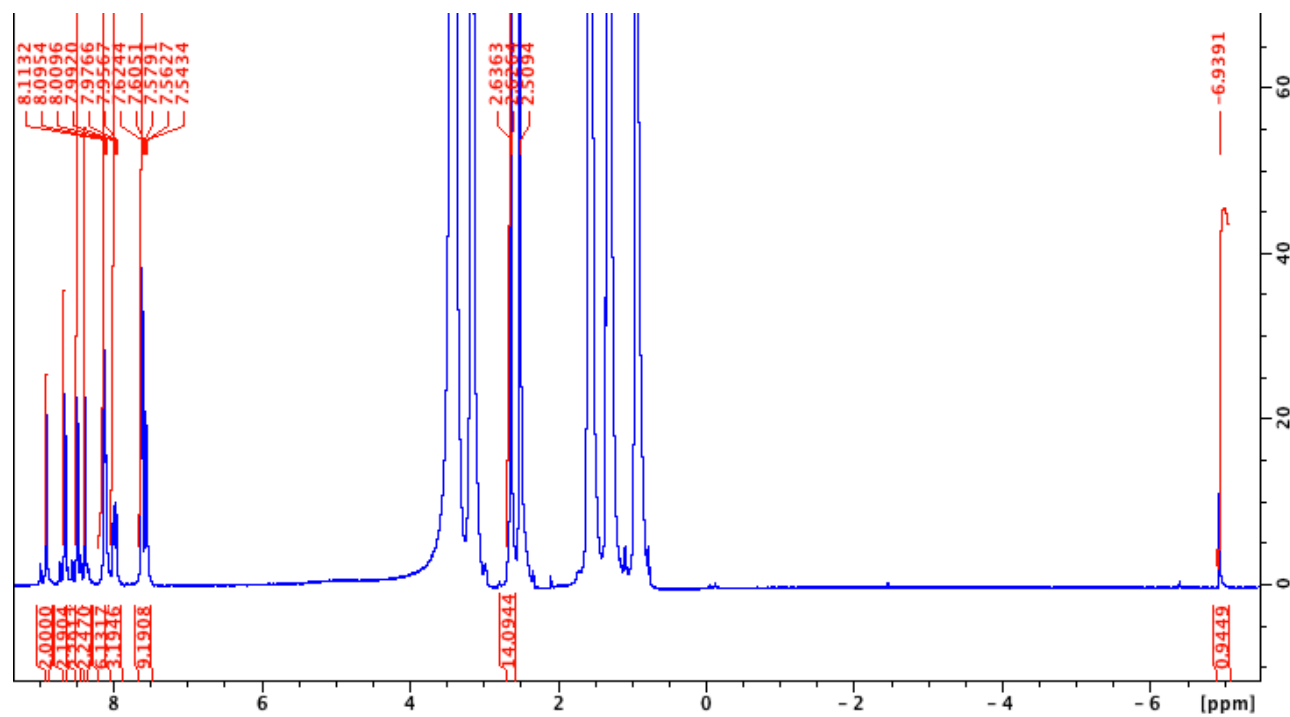


Figure S4. ^1H NMR spectrum of **1** in DMSO + Fluoride anion.

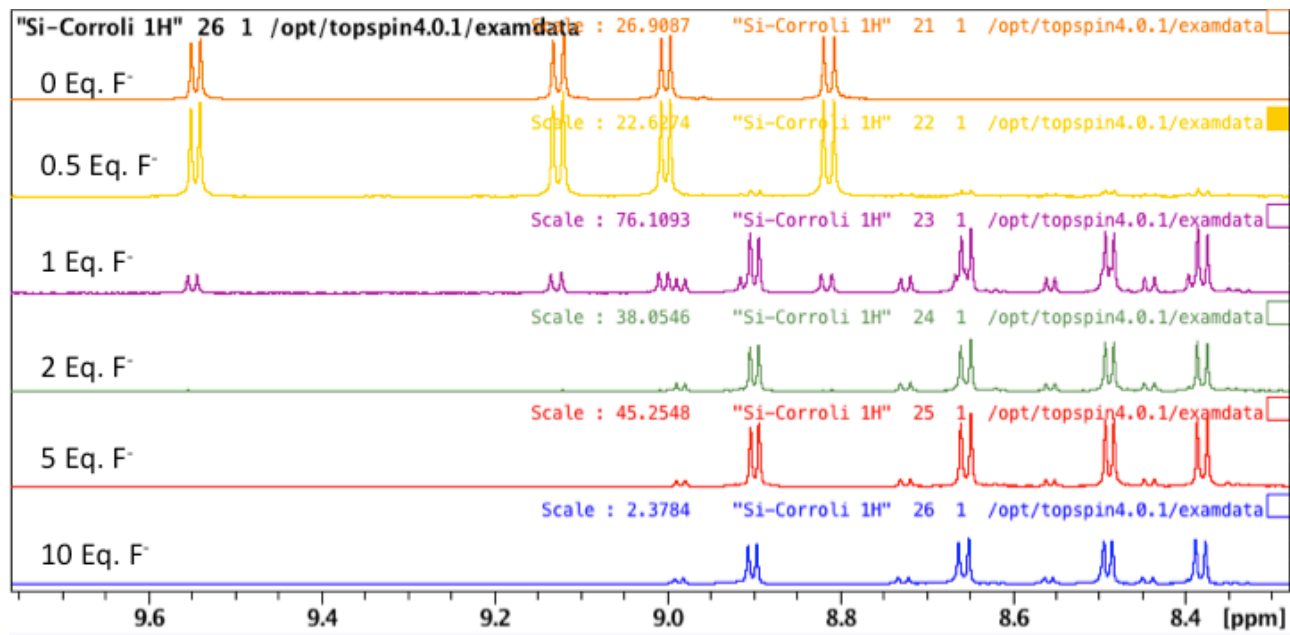


Figure S5. ¹H NMR Titration of **1** in DMSO with Fluoride ion: β-pyrrolic region.

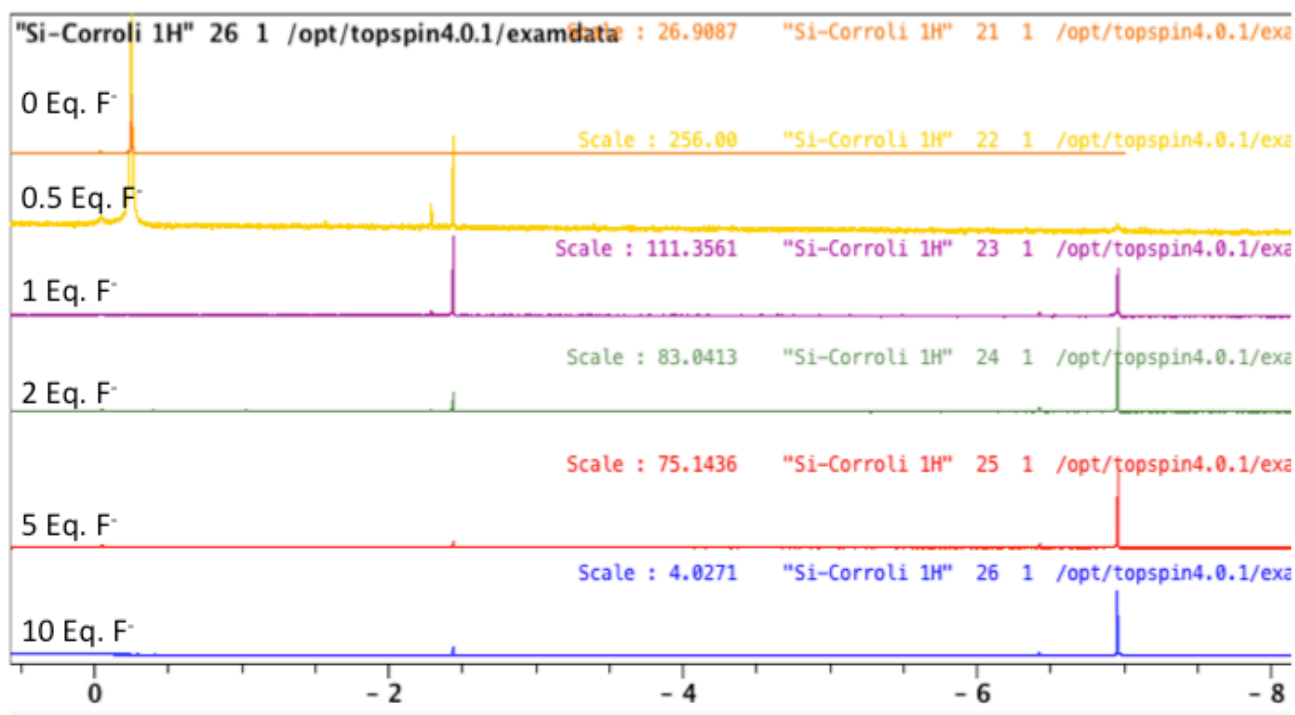


Figure S6. ¹H NMR Titration of **1** in DMSO with Fluoride ion: axial -OH region

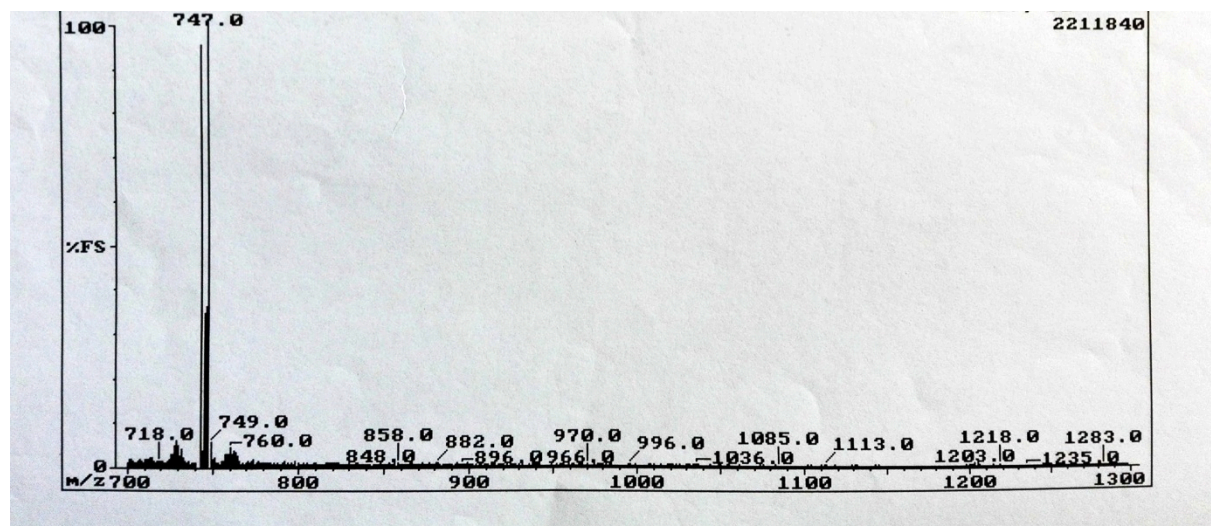


Figure S7. FAB mass spectrum of 1.

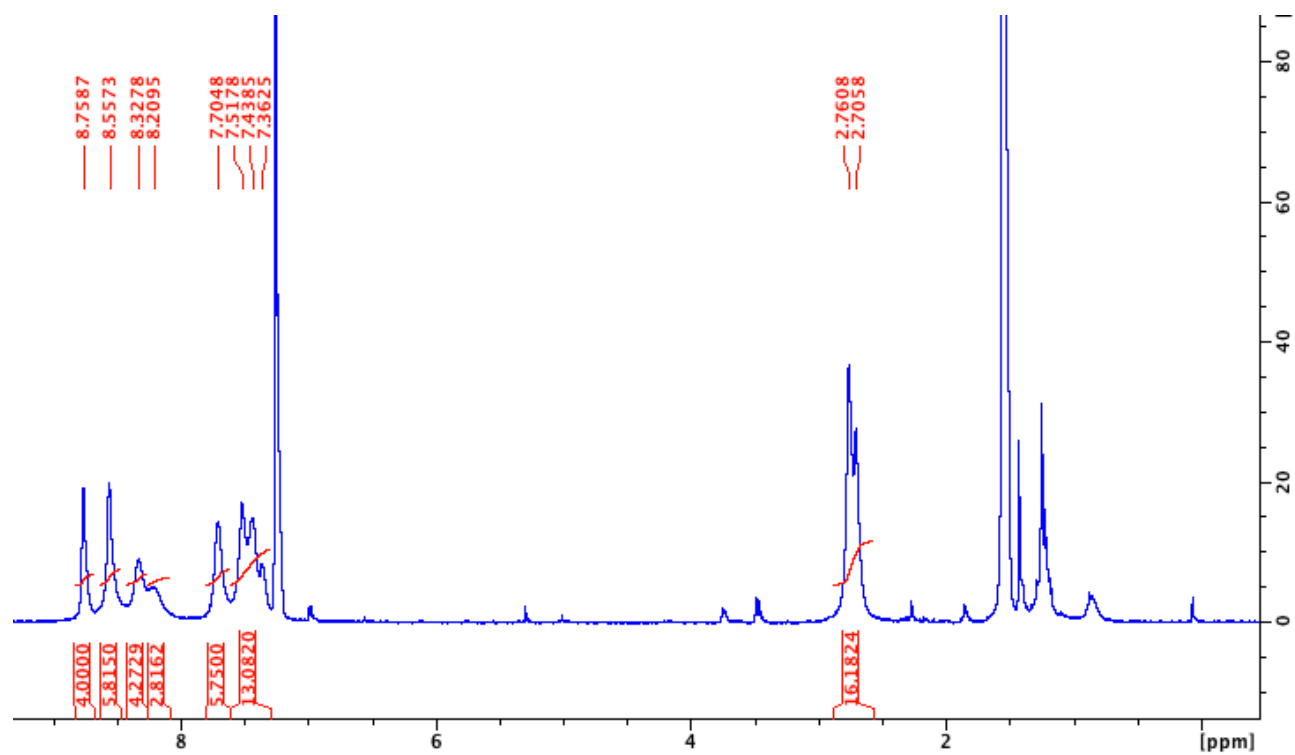


Figure S8. ^1H NMR spectrum of 2 in CDCl_3 .

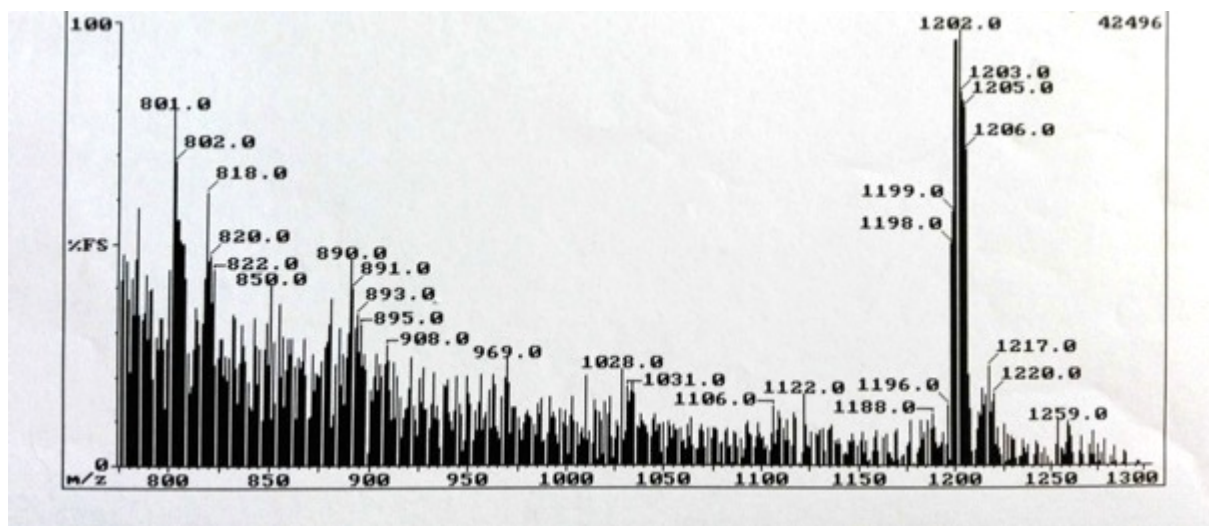


Figure S9. FAB mass spectrum of **2**.

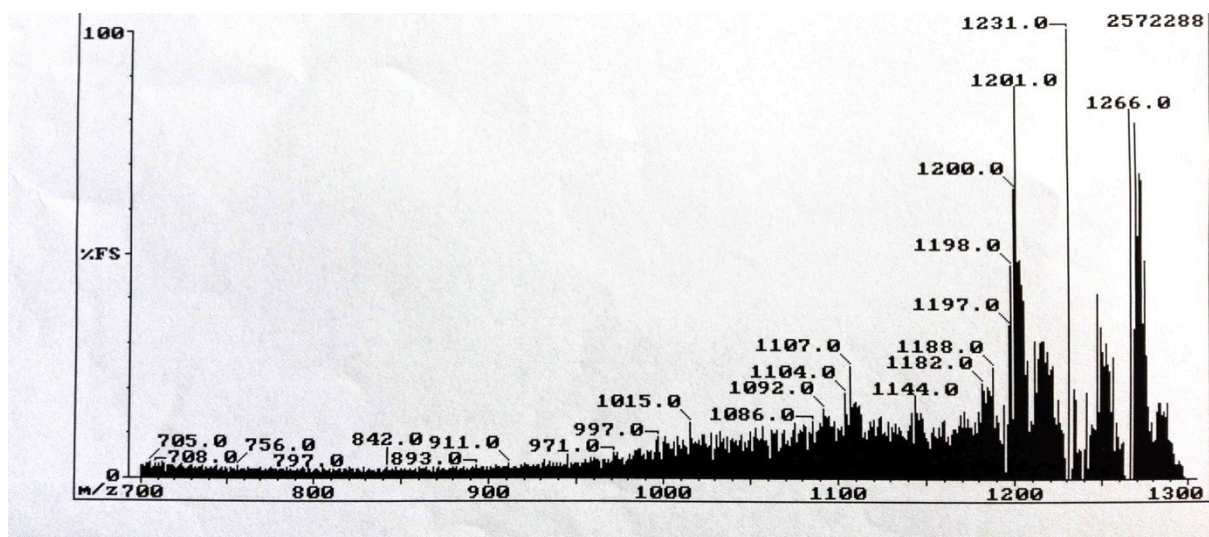


Figure S10. FAB mass spectrum of the products mixture after reaction of **2** with HCl.

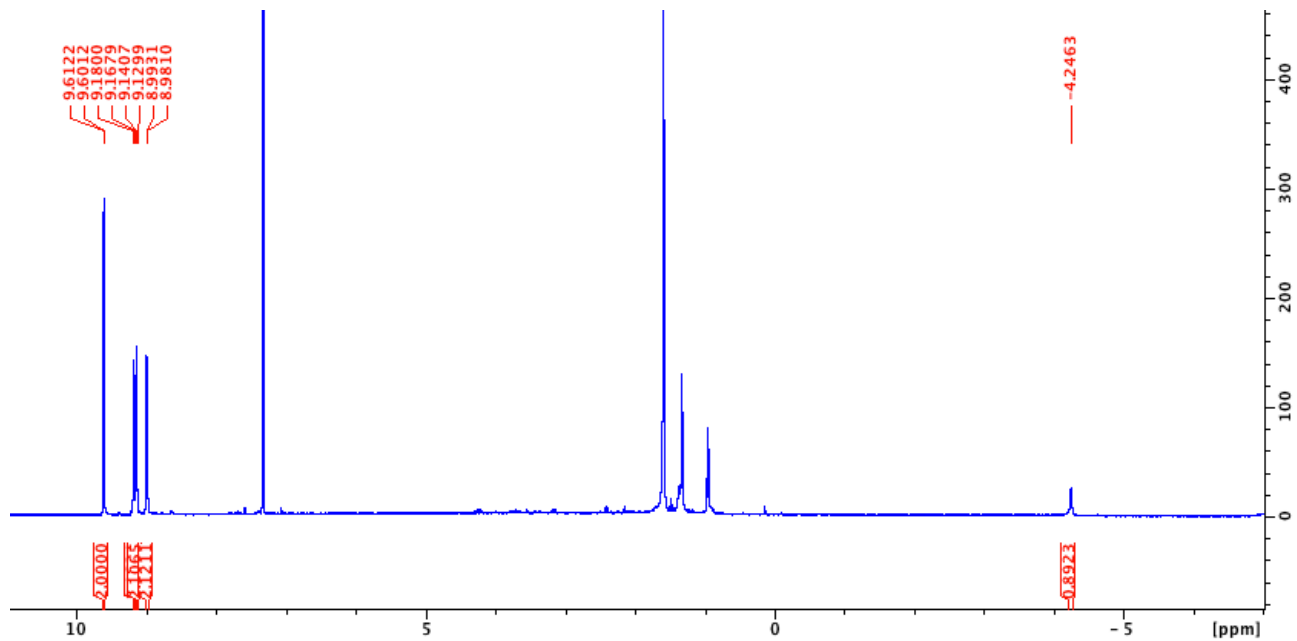


Figure S11. ^1H NMR spectrum of **3** in CDCl_3

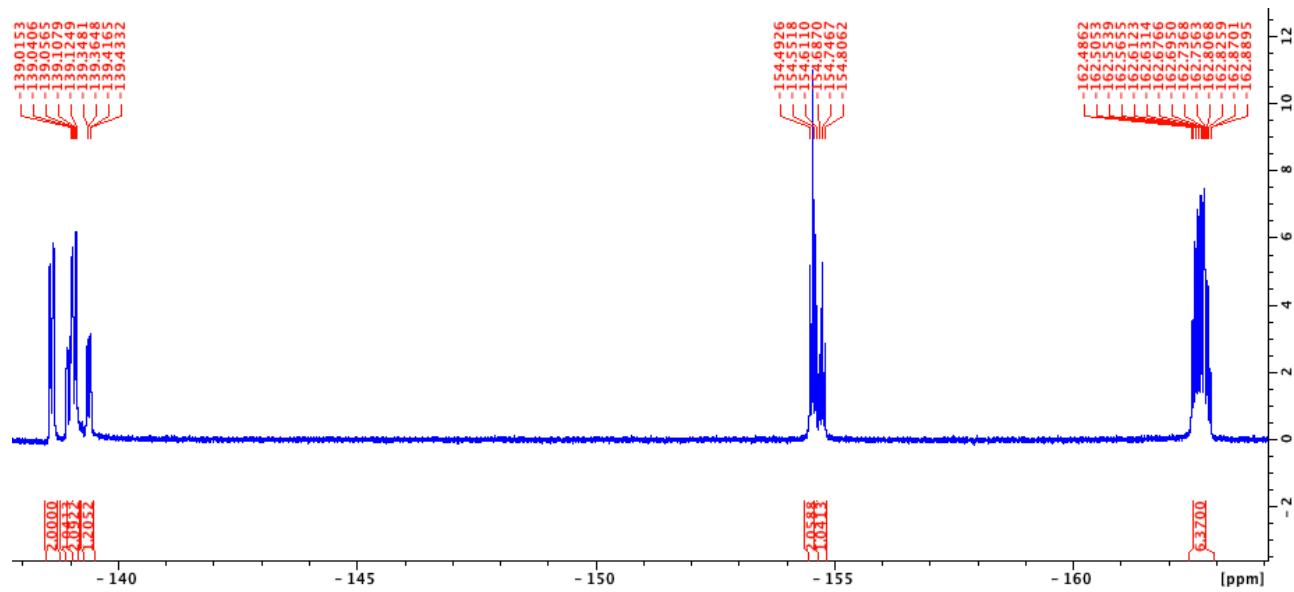


Figure S12. ^{19}F NMR spectrum of **3** in DMSO

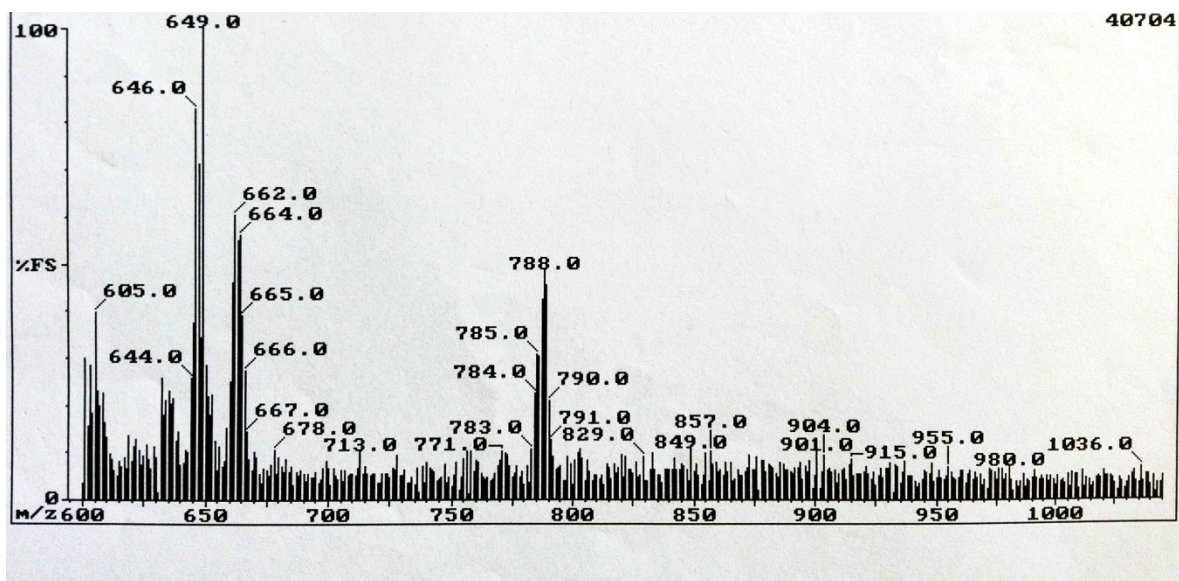


Figure S15. FAB mass spectrum of 4.

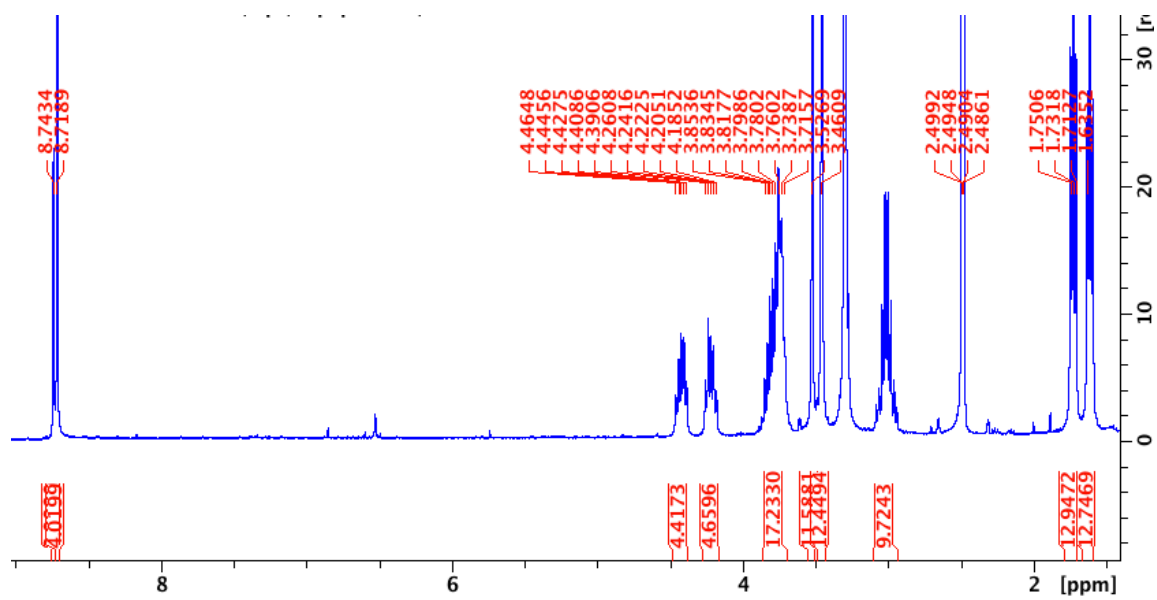


Figure S16. ¹H NMR spectrum of 5 in DMSO

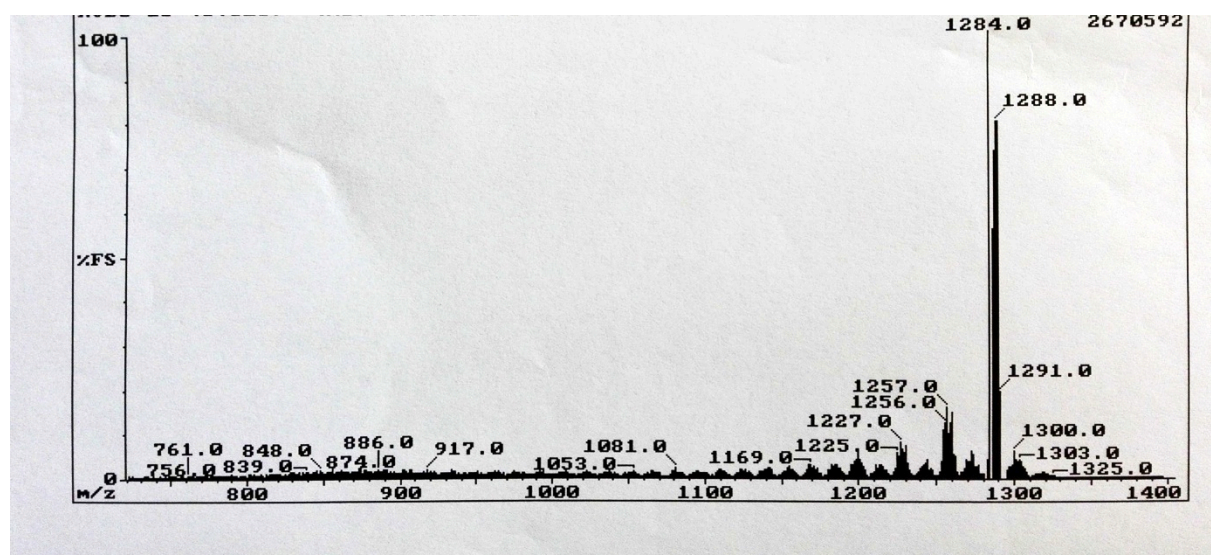


Figure S17. FAB mass spectrum of 5.

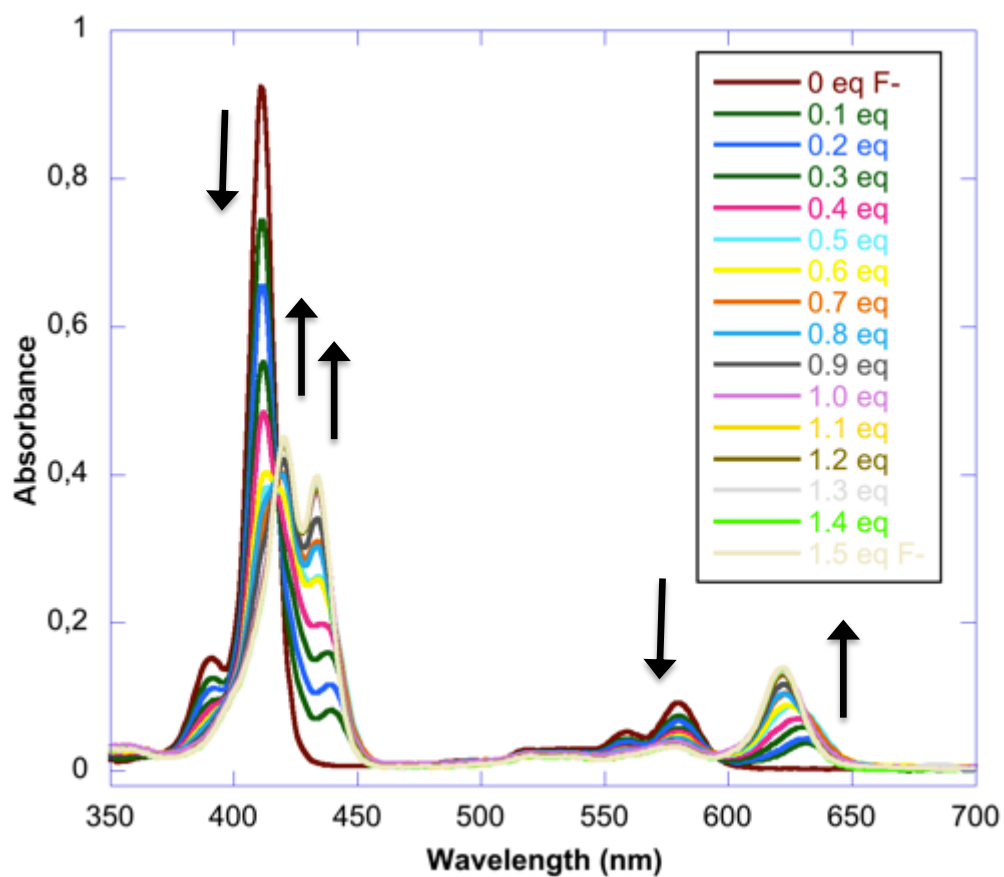


Figure S18. UV-vis spectral variation of 1 upon F⁻ titration

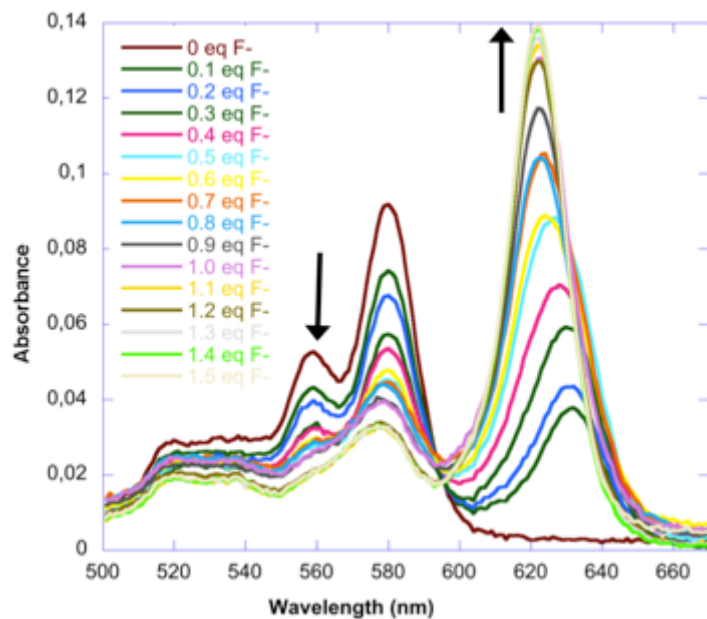


Figure S19. UV-vis spectral variation of **1** in the Q region upon F^- titration

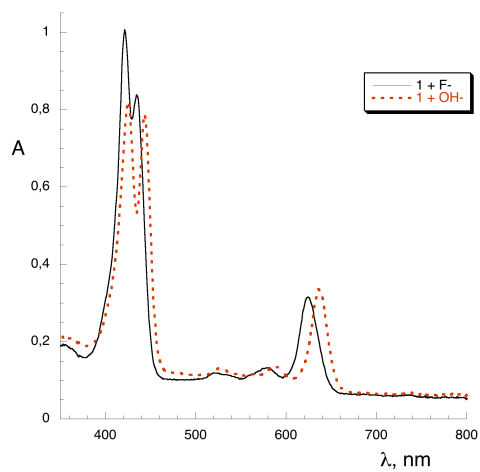


Figure S20. Comparison of the UV-vis spectral variations of **1** upon addition of F^- (black line) and OH^- (red dotted line)

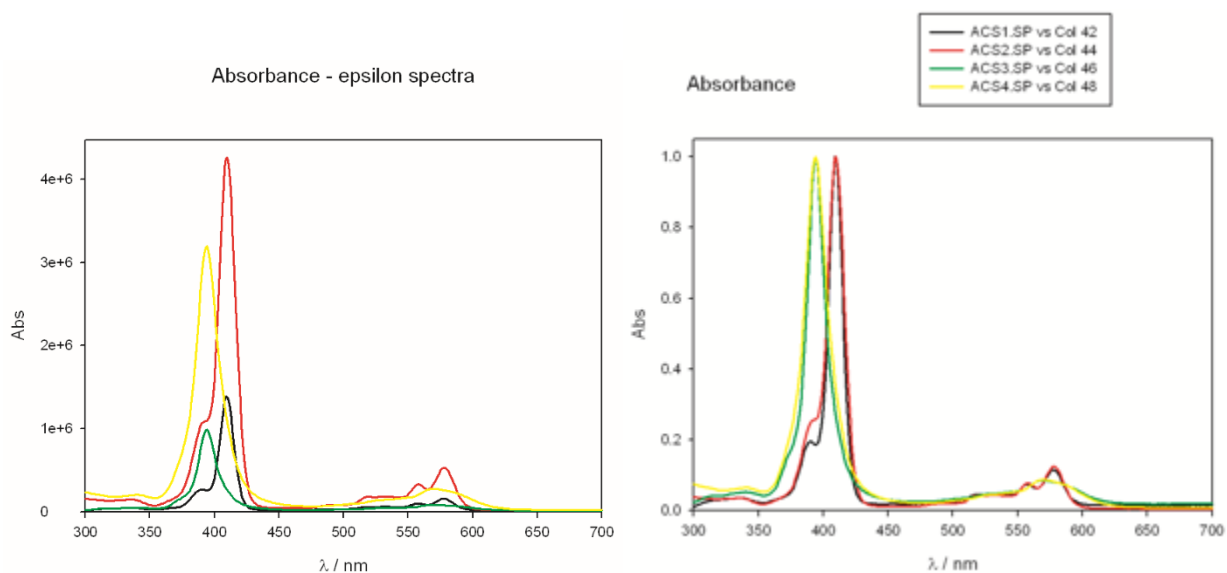


Figure S21. Absorption spectra of PluS NPs doped with **1** and **2** in water (samples **NP1L**, **NP1H**, **NP2L** and **NP2H** in black, red, green and yellow solid lines respectively), expressed as molar extinction coefficients (left) and normalized (right).

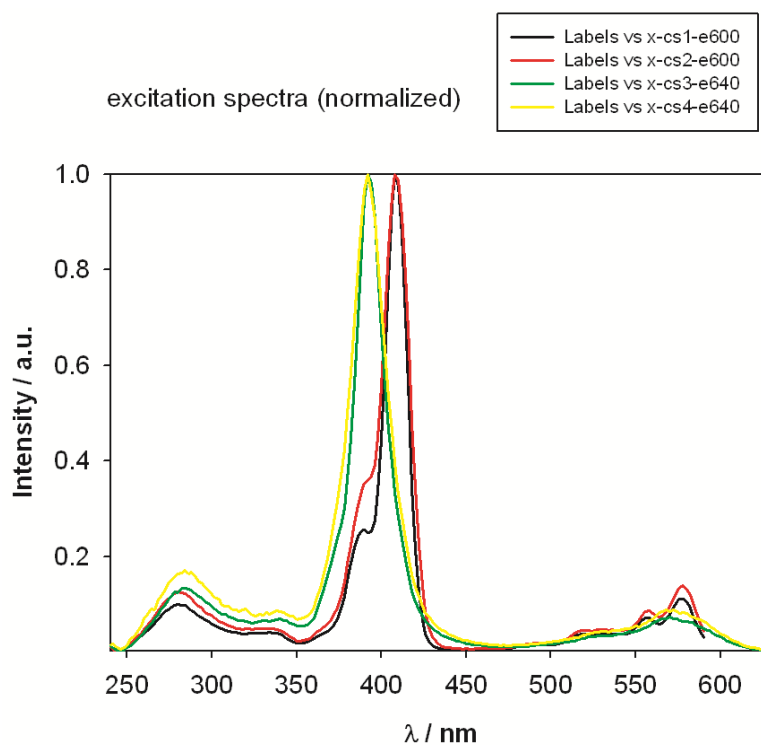


Figure S22. Excitation spectra of PluS NPs doped with corroles **1** and **2** in water (samples **NP1L**, **NP1H**, **NP2L** and **NP2H** in black, red, green and yellow solid lines respectively).

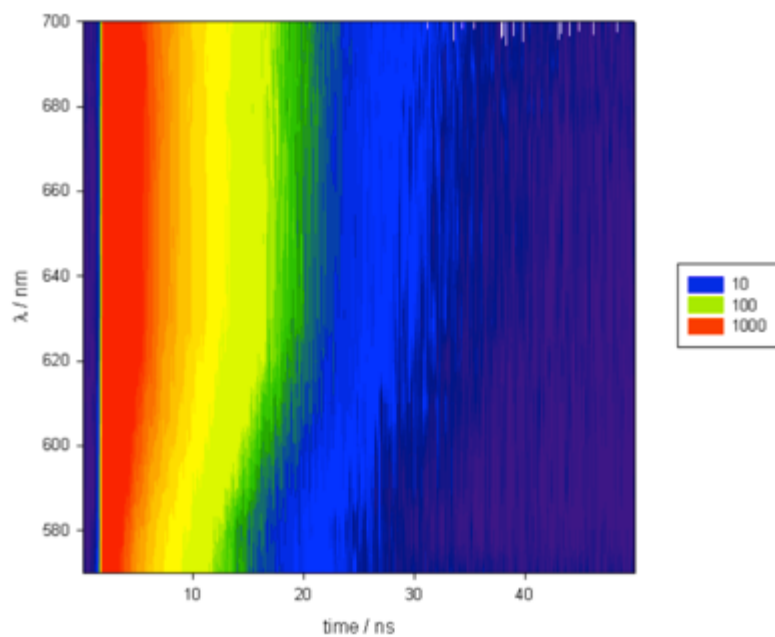


Figure S23. Time Resolved Emission Spectroscopy (TRES) of **NP2L** in bidimensional map (counts vs wavelength vs time). Acquisitions are performed with fixed counts at maximum, in order to obtain TRES normalized vs wavelength. Counts are in log scale.

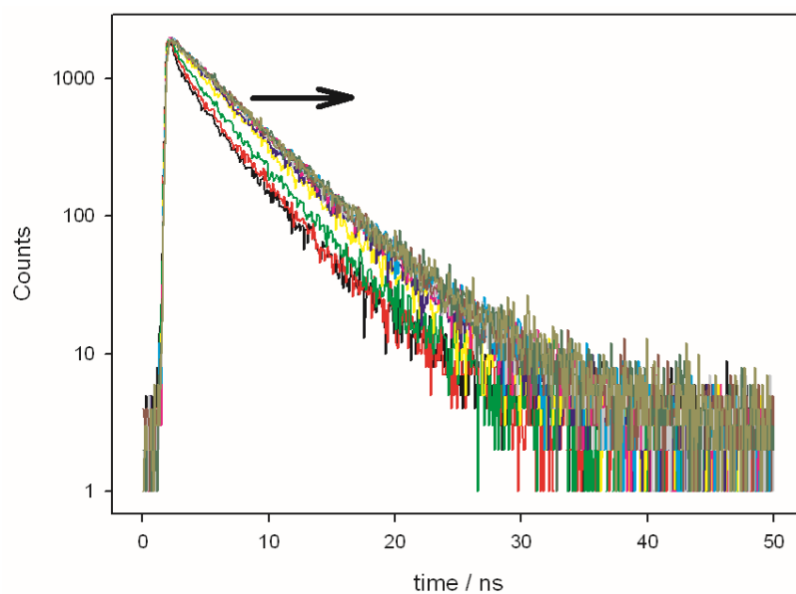


Figure S24. Plot of decays of TRES shown in previous figure

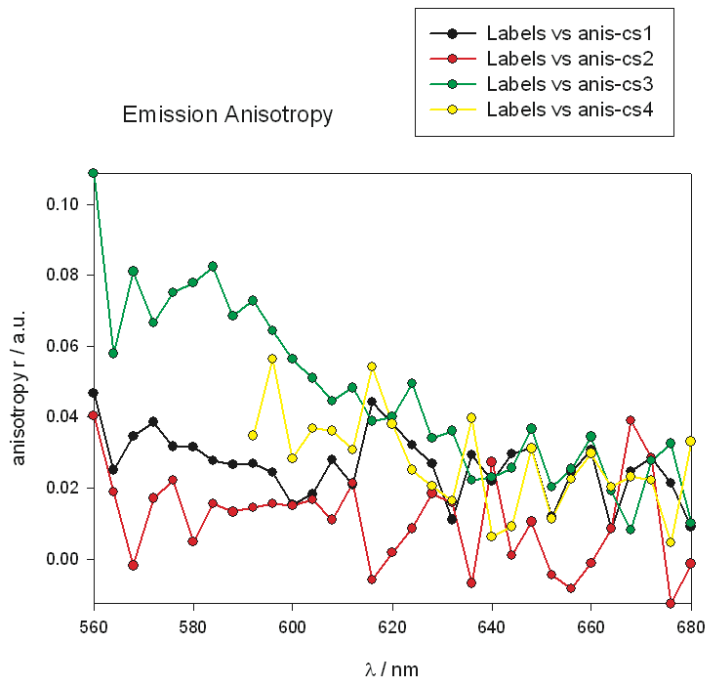


Figure S25. Emission anisotropy of samples **NP1L**, **NP1H**, **NP3L** and **NP3H**. Excitation wavelength 393 nm

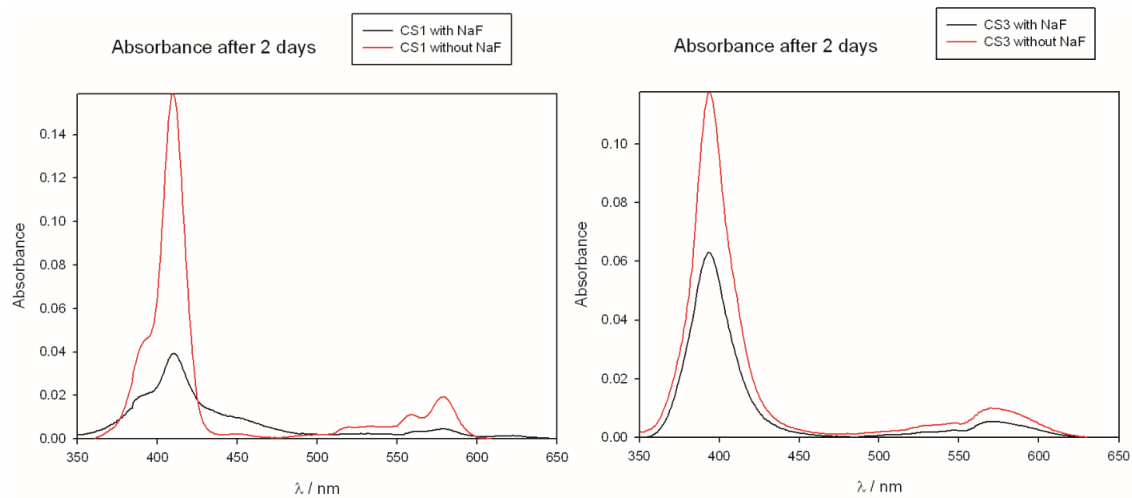


Figure S26. Absorbance spectra of samples **NP1L** (left) and **NP2L** (right) before (red) and 2 days after addition of NaF 50 mM (black).

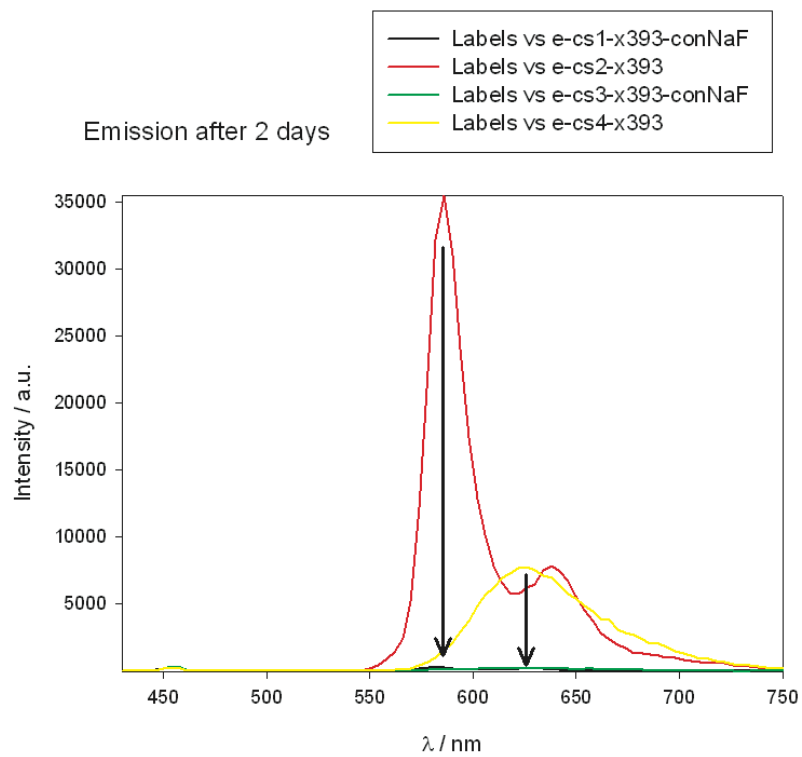


Figure S27. Emission spectra of samples **NP1L** and **NP2L** before (red and yellow) and 2 days after addition of NaF 50 mM (black and green).